

EXHAUST EMISSION PURIFICATION DEVICE FOR  
INTERNAL COMBUSTION ENGINE

5 BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an exhaust emission purification device for an internal combustion engine.

10 2. Description of the Related Art

Generally, in the case where an exhaust gas flowing into an exhaust emission purifier, carrying a NO<sub>x</sub> holding agent, contains a sulfur component (SO<sub>x</sub>, etc.), the exhaust emission purification capacity of the exhaust emission purifier is known to be deteriorated by sulfur poisoning.

In order to prevent the exhaust emission purification capacity of the exhaust emission purifier from being deteriorated due to sulfur poisoning, Japanese Unexamined Patent Publication No. 6-346768 discloses an exhaust emission purification device in which a sulfur component holding agent capable of holding the sulfur component in the exhaust gas flowing thereinto is arranged upstream of the exhaust emission purifier in the exhaust gas. In this exhaust emission purification device, when the sulfur component held by the sulfur component holding agent is released, the exhaust gas containing the released sulfur component is prevented from flowing into the exhaust emission purifier thereby to protect the exhaust emission purifier against the sulfur poisoning. As described above, an exhaust emission purification device having an exhaust emission purifier is required to avoid sulfur poisoning of the exhaust emission purifier.

35 With an exhaust emission purifier carrying a NO<sub>x</sub> holding agent, the air-fuel ratio of the exhaust gas flowing into the exhaust emission purifier is enriched by

a rich spike in order to release the NO<sub>x</sub> held in the NO<sub>x</sub> holding agent. When introducing the rich spike, i.e. when enriching the air-fuel ratio of the exhaust emission gas, fuel is required. The fuel consumed for the rich spike is desirably small in amount to minimize the fuel consumption. In the exhaust emission purification device described in the publication cited above, therefore, the amount of fuel consumption for the rich spike is required to be reduced as much as possible.

In view of this situation, the object of this invention is to provide an exhaust emission purification device for reducing the amount of fuel consumption while, at the same time, avoiding sulfur poisoning of a exhaust emission purifier.

#### SUMMARY OF THE INVENTION

According to one aspect of the invention, there is provided an exhaust emission purification device for an internal combustion engine, comprising a sulfur component holding agent arranged on the exhaust path of the internal combustion engine for holding the sulfur component, a NO<sub>x</sub> holding agent arranged downstream of the sulfur component holding agent in the exhaust gas for holding NO<sub>x</sub> and the sulfur components when the air-fuel ratio of the exhaust gas flowing thereinto is lean, and a reducing agent adding means for adding a reducing agent to the exhaust gas flowing into the NO<sub>x</sub> holding agent, wherein the concentration of the sulfur component contained in the reducing agent added by the reducing agent adding means is lower than the concentration of at least the sulfur component contained in the fuel supplied to a combustion chamber of the internal combustion engine.

In this aspect of the invention, the provision of the sulfur component holding agent upstream of the NO<sub>x</sub> holding agent in the exhaust gas substantially eliminates the sulfur component from the exhaust gas flowing into the NO<sub>x</sub> holding agent. Also, the sulfur component

contained in the reducing agent added to the exhaust gas flowing into the NO<sub>x</sub> holding agent is low in concentration. Thus, the inflow of the sulfur component into the NO<sub>x</sub> holding agent is suppressed. Further, the  
5 fuel of the required minimum amount to release NO<sub>x</sub> from the NO<sub>x</sub> holding agent can be added to the exhaust gas, thereby making it possible to suppress unnecessary fuel consumption. According to the first aspect of the invention, therefore, the amount of fuel consumption can  
10 be reduced while, at the same time, avoiding sulfur poisoning of the exhaust emission purifier.

According to another aspect of the invention, there is provided an exhaust emission purification device for an internal combustion engine, further comprising a  
15 bypass for bypassing the NO<sub>x</sub> holding agent and a flow rate regulation valve for controlling the flow rate of the exhaust gas flowing into the bypass, wherein the sulfur component holding agent holds the sulfur component in the exhaust gas flowing thereinto when the sulfur  
20 component holding conditions are satisfied, and releases the sulfur component held thereby when the sulfur component releasing conditions are satisfied, and wherein the sulfur component releasing conditions are caused to be satisfied and the greater part of the exhaust gas  
25 flows into the bypass when the sulfur component is released from the sulfur component holding agent.

In this aspect of the invention, the sulfur component holding conditions are satisfied, for example, in the case where the air-fuel ratio of the exhaust gas  
30 flowing into the sulfur component holding agent is lean or in the case where the air-fuel ratio of the exhaust gas flowing into the sulfur component holding agent is substantially equal to the stoichiometric air-fuel ratio or rich and, at the same time, the temperature of the  
35 sulfur component holding agent is lower than the sulfur component releasing temperature, while the sulfur component releasing conditions are satisfied, for

example, in the case where the air-fuel ratio of the exhaust gas flowing into the sulfur component holding agent is substantially equal to the stoichiometric air-fuel ratio or rich and, at the same time, the temperature of the sulfur component holding agent is higher than the sulfur component releasing temperature.

According to still another aspect of the invention, there is provided an exhaust emission purification device for an internal combustion engine, further comprising an annular path branching from the exhaust path and returning to the branching portion and a flow rate regulation valve for controlling the flow rate of the exhaust gas flowing into the annular path and the direction in which the exhaust gas flows into the annular path, wherein the sulfur component holding agent holds the sulfur component, in the exhaust gas flowing thereinto, when the sulfur component holding conditions are satisfied and releases the sulfur component held thereby when the sulfur component releasing conditions are satisfied, wherein a  $\text{NO}_x$  holding agent is arranged on the annular path and the flow regulation valve is arranged at the branching portion and wherein, when the sulfur component is released from the sulfur component holding agent, the sulfur component releasing conditions are caused to be satisfied and at the same time the flow rate regulation valve causes the greater part of the exhaust gas to flow through the exhaust path downstream of the branching portion without flowing into the annular path.

According to yet another aspect of the invention, there is provided an exhaust emission purification device for an internal combustion engine, wherein the reducing agent adding means is arranged on the annular path.

In the case where the reducing agent adding means is arranged upstream of the flow rate regulation valve in the exhaust gas, the reducing agent would be undesirably attached to the flow rate regulation valve. With the

exhaust emission purification device according to this aspect of the invention, in contrast, the reducing agent adding means is arranged on the annular path and, hence, downstream of the flow rate regulation valve in the exhaust gas, thereby making it possible to avoid the problem that the reducing agent would or might be attached to the flow rate regulation valve.

According to a further aspect of the invention, there is provided an exhaust emission purification device for an internal combustion engine, wherein the greater part of the exhaust gas flows into the annular path from the exhaust path in such a manner as to flow in one direction through the annular path in the case where the flow rate regulation valve is in a first working position and, the greater part of the exhaust gas flows into the annular path from the exhaust path in such a manner as to flow in the opposite direction through the annular path in the case when the flow rate regulation valve is in a second working position.

According to a still further aspect of the invention, there is provided an exhaust emission purification device for an internal combustion engine, wherein the  $\text{NO}_x$  holding agent is carried on a particulate filter capable of trapping the particulates contained in the exhaust gas flowing thereinto.

According to a yet further aspect of the invention, there is provided an exhaust emission purification device for an internal combustion engine, wherein the concentration of the sulfur component contained in the reducing agent is substantially zero.

According to a further aspect of the invention, there is provided an exhaust emission purification device for an internal combustion engine, wherein the reducing agent is light oil or methane.

According to a still further aspect of the invention, there is provided an exhaust emission purification device for an internal combustion engine,

wherein the reducing agent is stored in a tank different from the tank for storing the fuel supplied to the combustion chamber of the internal combustion engine.

5 According to a yet further aspect of the invention, there is provided an exhaust emission purification device for an internal combustion engine, wherein the reducing agent is changed in quality from the fuel supplied to the combustion chamber of the internal combustion engine.

10 According to a further aspect of the invention, there is provided an exhaust emission purification device for an internal combustion engine, comprising a tank having two fuel supply paths including a fuel supply path for supplying the fuel to the combustion chamber of the internal combustion engine and a fuel supply path for  
15 supplying the fuel to the reducing agent adding means, and a desulfurizing unit for changing the quality of the fuel, arranged in the fuel supply path for supplying the fuel to the reducing agent adding means.

#### BRIEF DESCRIPTION OF THE DRAWINGS

20 The present invention may be more fully understood from the description of the preferred embodiments of the invention set forth below, together with the accompanying drawings in which:

25 Fig. 1 is a schematic view showing the whole of an internal combustion engine comprising an exhaust emission purification device according to the invention;

Fig. 2 is a schematic view showing an exhaust emission purification device according to a first embodiment of the invention;

30 Figs. 3A-3C are a schematic views showing an exhaust emission purification device according to a second embodiment of the invention;

35 Fig. 4 is a schematic view showing an exhaust emission purification device according to a third embodiment of the invention;

Fig. 5 is a schematic view showing an exhaust emission purification device according to a fourth

embodiment of the invention; and

Figs. 6A and 6B are a views for explaining the operation of removing the fine particles.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

5       An exhaust emission purification device according to the invention will be explained below with reference to the drawings. Fig. 1 shows a compression ignition diesel engine of an in-cylinder injection type having an exhaust emission purification device according to the invention.  
10       The exhaust emission purification device according to the invention is applicable also to an internal combustion engine of a spark-ignition type.

Referring to Figs. 1 and 2, reference numeral 1 designates an engine body, numeral 2 a cylinder block,  
15       numeral 3 a cylinder head, numeral 4 a piston, numeral 5 a combustion chamber, numeral 6 an electrically-controlled fuel injector, numeral 7 an intake valve, numeral 8 an intake port, numeral 9 an exhaust valve and numeral 10 an exhaust port. The intake port 8 is  
20       connected to a surge tank 12 through a corresponding intake branch pipe 11, and the surge tank 12 is connected to a compressor 15 of an exhaust turbocharger 14 through an intake duct 13.

Inside the intake duct 13 is arranged a throttle  
25       valve 17 driven by a step motor 16. Further, a cooling unit 18 is arranged around the intake duct 13 for cooling the intake air flowing in the intake duct 13. In the internal combustion engine shown in Fig. 1, the engine coolant water is led into the cooling unit 18 and the  
30       intake air is cooled by the engine coolant water. On the other hand, the exhaust port 10 is connected to an exhaust turbine 21 of the exhaust turbocharger 14 through an exhaust manifold 19 and an exhaust pipe 20, and the outlet of the exhaust turbine 21 is connected to the  
35       exhaust emission purification device 23, described in detail below, through an exhaust pipe 22.

The exhaust manifold 19 and the surge tank 12 are

connected to each other through an exhaust gas recirculation (hereinafter referred to as EGR) path 24. An electrically-controlled EGR control valve 25 is arranged in the EGR path 24. An EGR cooling unit 26 is  
5 arranged around the EGR path 24 for cooling the EGR gas flowing in the EGR path 24. In the internal combustion engine shown in Fig. 1, the engine coolant water is guided into the EGR cooling unit 26 and the EGR gas is cooled.

10 The fuel injectors 6 are connected to a fuel reservoir, a common rail 27, through fuel supply pipes 6a. The fuel is supplied into the common rail 27 from an electrically-controlled variable-discharge fuel pump 28. The fuel supplied into the common rail 27 is supplied to  
15 the fuel injectors 6 through fuel supply pipes 6a. A fuel pressure sensor 29 is mounted on the common rail 27 for detecting the fuel pressure in the common rail 27. The discharge amount of the fuel pump 28 is controlled based on the output signal of the fuel pressure sensor 29  
20 so that the fuel pressure in the common rail 27 reaches a target fuel pressure.

The electronic control unit (ECU) 40 includes a digital computer which, in turn, has a ROM (read-only memory) 42, a RAM (random access memory) 43, a CPU  
25 (microprocessor) 44, an input port 45 and an output port 46 connected to each other through a bidirectional bus 41. The output signal of the fuel pressure sensor 29 is input to the input port 45 through a corresponding A/D converter 47.

30 An accelerator pedal 51 is connected with a load sensor 52 for generating an output voltage proportional to the amount of depression of the acceleration pedal 51. The output voltage of the load sensor 52 is input to the input port 45 through a corresponding A/D converter 47.  
35 Further, the input port 45 is connected to a crank angle sensor 53 for generating an output pulse each time a crankshaft rotates by for example 30 degrees. The output



port 46, on the other hand, is connected with the fuel injection valve 6, the step motor 16, the EGR control valve 25 and the fuel pump 28 through a corresponding drive circuit 48.

5           Next, the configuration of the exhaust emission purification device 23 according to the invention will be explained with reference to Fig. 2. The exhaust emission purification device 23 according to the invention comprises a sulfur component holding agent 61 capable of  
10           holding a sulfur component ( $\text{SO}_x$ , etc.) of the exhaust gas flowing thereinto and an  $\text{NO}_x$  holding agent 62 capable of holding the components other than the sulfur component of the exhaust gas flowing thereinto or, especially,  $\text{NO}_x$  in the exhaust gas.

15           The sulfur component holding agent 61 is built into a casing 64 arranged on the exhaust pipe (engine exhaust path) 63 connected to the outlet of the exhaust turbine 21. The sulfur component holding agent 61 is provided with a temperature sensor 65 for detecting the  
20           temperature of the sulfur component holding agent 61. The temperature sensor 65 is connected to the input port 45 of the ECU 40 through a corresponding A/D converter 47. An exhaust pipe 66 is arranged downstream of the exhaust pipe 63 in the exhaust gas. The exhaust pipe 66  
25           includes an upstream exhaust pipe 66a a branch portion 66b, a holding agent-side branch pipe 66c, a bypass-side branch pipe (bypass) 66d and a downstream exhaust pipe 66e. The  $\text{NO}_x$  holding agent 62 is built into the casing 67 arranged on the holding agent-side branch pipe 66c.

30           The exhaust pipe 66 will be described in more detail. The upstream exhaust pipe 66a is connected to the exhaust pipe 63 arranged upstream of the exhaust pipe 66. The upstream exhaust pipe 66a branches at the branching portion 66 into the holding agent-side branch  
35           pipe 66c and the bypass-side branch pipe 66d for bypassing the  $\text{NO}_x$  holding agent 62. The branch pipes 66c, 66d merge with each other downstream of the  $\text{NO}_x$

holding agent 62 in the exhaust gas. A flow rate regulation valve 68 is arranged at the branching portion 66b. The flow rate regulation valve 68 is controlled by the step motor 69 which is connected to the output port 46 of the ECU 40 through a corresponding drive circuit 48.

The flow rate regulation valve 68 is capable of regulating the flow rate of the exhaust gas flowing into the bypass-side branch pipe 66d. Especially, in accordance with the operating position thereof, the flow rate regulation valve 68 can regulate the ratio between the flow rate of the exhaust gas flowing into the holding agent-side branch pipe 66c and the flow rate of the exhaust gas flowing into the bypass-side branch pipe 66d. For example, the flow rate regulation valve 68 can pivot between the position for closing the bypass-side branch pipe 66d (the position indicated by the solid line in Fig. 2) and the bypass position for bypassing the NO<sub>x</sub> holding agent 62 by closing the holding agent-side branch pipe 66c (the position indicated by dashed line), and determines the flow rate of the exhaust gas flowing into each of the branch pipes 66c, 66d in accordance with the angle  $\theta$  from the position at which the holding agent-side branch pipe 66c is closed.

The exhaust emission purification device 23 according to the first embodiment further comprises a reducing agent adding unit (reducing agent adding means) 70 arranged in the holding agent-side branch pipe 66c downstream of the flow rate regulation valve 68 upstream of the NO<sub>x</sub> holding agent 62 in the exhaust gas. The reducing agent adding unit 70 adds a reducing agent to the exhaust gas flowing into the NO<sub>x</sub> holding agent 62. More specifically, the reducing agent adding unit 70 is arranged in proximity to the NO<sub>x</sub> holding agent 62 so as to inject the reducing agent toward the NO<sub>x</sub> holding agent 62. The reducing agent adding unit 70 is connected to the output port 46 of the ECU 40 through a corresponding

drive circuit 48, so that the amount of the reducing agent added to the exhaust gas is regulated based on the signal transmitted from the ECU 40. Incidentally, according to this embodiment, a fuel having a similar composition to the fuel supplied to the combustion chamber of the internal combustion engine is used as a reducing agent. Although an explanation is given on the assumption that the fuel is added to the exhaust gas from the reducing agent adding unit 70, a fuel of a composition different to the fuel supplied to the combustion chamber or any reducing agent different from the fuel may be used with equal effect.

The ratio of the air to the fuel supplied to the exhaust path upstream of the NO<sub>x</sub> holding agent 62, the combustion chamber 5 and the intake path is referred to as the air-fuel ratio of the exhaust gas. The NO<sub>x</sub> holding agent 62 of the exhaust emission purification device 23 holds the NO<sub>x</sub> in the exhaust gas when the air-fuel ratio of the exhaust gas flowing thereinto is lean, and releases the NO<sub>x</sub> held thereby when the oxygen concentration of the exhaust gas flowing thereinto decreases. Further, in the case where the oxygen concentration of the exhaust gas flowing into the NO<sub>x</sub> holding agent 62 is low and the exhaust gas flowing thereinto contains the reducing agent, the NO<sub>x</sub> released from the NO<sub>x</sub> holding agent 62 is reduced and purified.

This NO<sub>x</sub> holding agent 62 is unable to hold NO<sub>x</sub> any further when the amount of NO<sub>x</sub> held thereby increases. Specifically, in the case where the air-fuel ratio of the exhaust gas flowing into the NO<sub>x</sub> holding agent 62 continues to be lean, the NO<sub>x</sub> holding capacity of the NO<sub>x</sub> holding agent 62 decreases and then the NO<sub>x</sub> holding agent 62 is unable to hold NO<sub>x</sub> any longer, with the result that the exhaust gas that has passed through the NO<sub>x</sub> holding agent 62 still contains NO<sub>x</sub>. In the case where the amount of NO<sub>x</sub> held by the NO<sub>x</sub> holding agent 62 exceeds a predetermined amount, therefore, it is a common practice

to carry out the rich spike operation in which an exhaust gas having a low oxygen concentration and containing a large amount of reducing agent is introduced into the NO<sub>x</sub> holding agent 62 thereby to release and reduce the NO<sub>x</sub> held in the NO<sub>x</sub> holding agent 62.

More specifically, the NO<sub>x</sub> sensor 71 mounted upstream of the NO<sub>x</sub> holding agent 62 in the exhaust gas detects the amount of NO<sub>x</sub> in the exhaust gas flowing into the NO<sub>x</sub> holding agent 62 thereby to estimate the amount of NO<sub>x</sub> held by the NO<sub>x</sub> holding agent 62. Once the estimated amount of NO<sub>x</sub> increases beyond a predetermined amount, i.e. in the case where the NO<sub>x</sub> holding capacity of the NO<sub>x</sub> holding agent 62 decreases, the fuel is added, as a reducing agent, to the exhaust gas flowing into the NO<sub>x</sub> holding agent 62, from the reducing agent adding unit 70 mounted upstream of the NO<sub>x</sub> holding agent 62 in the exhaust gas, as a rich spike operation. The amount of the fuel added by the reducing agent adding unit 70 is sufficient to decrease the oxygen concentration of the exhaust gas flowing into the NO<sub>x</sub> holding agent 62 and to reduce the NO<sub>x</sub> released from the NO<sub>x</sub> holding agent 62 at the same time. As the result of carrying out the rich spike operation, substantially all the NO<sub>x</sub> held in the NO<sub>x</sub> holding agent 62 is released and reduced, thereby restoring the NO<sub>x</sub> holding capacity of the NO<sub>x</sub> holding agent 62.

On the other hand, the NO<sub>x</sub> holding agent 62 holds not only NO<sub>x</sub> but also the sulfur component in the exhaust gas flowing thereinto. Once the sulfur component is held in the NO<sub>x</sub> holding agent 62, the NO<sub>x</sub> holding capacity of the NO<sub>x</sub> holding agent 62 is decreased. The fact that the NO<sub>x</sub> holding capacity of the NO<sub>x</sub> holding agent 62 is decreased by the sulfur component being held by the NO<sub>x</sub> holding agent 62 is called "sulfur poisoning" of the NO<sub>x</sub> holding agent 62. More specifically, with an increase in the amount of the sulfur component held by the NO<sub>x</sub> holding agent 62, the amount of NO<sub>x</sub> which can be held by

the NO<sub>x</sub> holding agent 62 decreases. In other words, with the progress of the sulfur poisoning of the NO<sub>x</sub> holding agent 62, the NO<sub>x</sub> holding ability of the NO<sub>x</sub> holding agent 62 decreases.

5           Generally, therefore, once the NO<sub>x</sub> holding agent 62 is sulfur-poisoned, the regeneration process of the sulfur poisoning is carried out to release the sulfur component from the NO<sub>x</sub> holding agent 62. Normally, for releasing the sulfur component held in the NO<sub>x</sub> holding agent 62, the air-fuel ratio of the exhaust gas flowing into the NO<sub>x</sub> holding agent 62 must be enriched and, at the same time, the temperature of the NO<sub>x</sub> holding agent 62 must be raised beyond the sulfur releasing temperature (say, about 650 °C).

15           In the diesel engine of a compression ignition type, however, the temperature of the exhaust gas flowing into the NO<sub>x</sub> holding agent 62 during the normal engine operation is much lower than the sulfur releasing temperature of the NO<sub>x</sub> holding agent 62. To carry out the regeneration process of the sulfur poisoning for the NO<sub>x</sub> holding agent 62, therefore, the internal combustion engine is required to be controlled in a special manner to increase the temperature of the exhaust gas discharged from the internal combustion engine. When the NO<sub>x</sub> holding agent 62 reaches a temperature higher than the sulfur releasing temperature, on the other hand, the NO<sub>x</sub> holding agent 62 is thermally degraded and the NO<sub>x</sub> holding capacity thereof is decreased. Also, in the case where the NO<sub>x</sub> holding agent 62 contains a catalyst substance for oxidizing the components of the exhaust gas, the performance, such as the ability to oxidize the catalyst substance, is reduced by the heat. Further, releasing the sulfur component from the NO<sub>x</sub> holding agent 62 consumes a comparatively long time and, therefore, the air-fuel ratio of the exhaust gas flowing into the NO<sub>x</sub> holding agent 62 is required to be kept rich over a comparatively long period, with the result that the fuel

consumption is increased and the fuel cost is considerably increased. Also, in the case where the NO<sub>x</sub> holding agent 62 is carried on the particulate filter (hereinafter referred to as the filter), as described  
5 later, the particulates, which may be trapped in the filter in a large amount, would be ignited if the temperature of the filter 62 is raised beyond the sulfur releasing temperature. As a result, the temperature of filter 62 would increase to such an extent as to melt or develop  
10 cracks in the filter.

In view of this, with the exhaust emission purification device 23 shown in Figs. 1 and 2, a sulfur component holding agent 61 for holding the sulfur component of the exhaust gas flowing thereinto is  
15 arranged upstream of the NO<sub>x</sub> holding agent 62 in the exhaust gas so that an exhaust gas substantially free of the sulfur component flows into the NO<sub>x</sub> holding agent 62. As a result, it becomes difficult for the sulfur component to flow into the NO<sub>x</sub> holding agent 62 during  
20 the normal operation of the internal combustion engine, or especially, during other than the rich spike operation for the NO<sub>x</sub> holding agent 62. This decreases the number of times the regeneration process of the sulfur poisoning is required to be carried out for the NO<sub>x</sub> holding agent  
25 62.

In the exhaust emission purification device 23 shown in Figs. 1 and 2, the fuel added to the exhaust gas from the reducing agent adding unit 70 arranged upstream of the NO<sub>x</sub> holding agent 62 in the exhaust gas flows  
30 directly into the NO<sub>x</sub> holding agent 62 during the rich spike operation for releasing NO<sub>x</sub> from the NO<sub>x</sub> holding agent 62. Generally, the fuel contains a sulfur component. If the added fuel flows directly into the NO<sub>x</sub> holding agent 62, therefore, the sulfur component of the  
35 fuel comes to be held by the NO<sub>x</sub> holding agent 62, thereby undesirably promoting the sulfur poisoning of the NO<sub>x</sub> holding agent 62.

With the exhaust emission purification device 23 according to the first embodiment of the invention, in contrast, the concentration of the sulfur component contained in the fuel added from the reducing agent adding unit 70 to the exhaust gas flowing into the NO<sub>x</sub> holding agent 62 is lower than that of the sulfur component in the fuel supplied to the combustion chamber 5 of the internal combustion engine. Specifically, the reducing agent adding unit 70 adds a fuel of a low sulfur component concentration to the exhaust path upstream of the NO<sub>x</sub> holding agent 62 but downstream of the sulfur component holding agent 61 in the exhaust gas. By doing so, even in the case where the fuel is added from the reducing agent adding unit 70 such as when carrying out the rich spike operation for the NO<sub>x</sub> holding agent 62, for example, the amount of the sulfur component contained in the exhaust gas flowing into the NO<sub>x</sub> holding agent 62 is comparatively small and, therefore, the progress of the sulfur poisoning of the NO<sub>x</sub> holding agent 62 is prevented.

Especially in the case where the concentration of the sulfur component of the fuel added from the reducing agent adding unit 70 to the exhaust gas flowing into the NO<sub>x</sub> holding agent 62 is substantially zero, substantially no sulfur component flows into the NO<sub>x</sub> holding agent 62 when carrying out the rich spike operation against the NO<sub>x</sub> holding agent 62. Also, during a period other than the rich spike operation for the NO<sub>x</sub> holding agent 62, substantially all the sulfur component of the exhaust gas discharged from the internal combustion engine is removed by the sulfur component holding agent 61 and, therefore, substantially no sulfur component flows into the NO<sub>x</sub> holding agent 62. Thus, in the case where the concentration of the sulfur component of the fuel added from the reducing agent adding unit 70 is substantially zero, substantially no sulfur component flows into the NO<sub>x</sub> holding agent 62 and, therefore, the requirement for

the regeneration process of the sulfur poisoning for the NO<sub>x</sub> holding agent 62 is substantially eliminated.

According to the first embodiment of the invention, the sulfur component holding agent 61 holds the sulfur component in the exhaust gas flowing thereinto when the sulfur component holding conditions are satisfied, and releases the sulfur component when the sulfur component releasing conditions are satisfied. More specifically, in the case where the air-fuel ratio of the exhaust gas flowing into the sulfur component holding agent 61 is lean or in the case where the air-fuel ratio of the exhaust gas flowing into the sulfur component holding agent 61 is substantially equal to the stoichiometric air-fuel ratio or rich with the temperature of the sulfur component holding agent 61 lower than the sulfur component releasing temperature, then the sulfur component holding agent 61 holds the sulfur component in the exhaust gas while, in the case where the air-fuel ratio of the exhaust gas flowing into the sulfur component holding agent 61 is rich and the temperature of the sulfur component holding agent 61 is higher than the sulfur component releasing temperature, on the other hand, the sulfur component holding agent 61 releases the sulfur component held thereby.

In this sulfur component holding agent 61, the amount of the sulfur component capable of being held is reduced with an increase in the amount of the sulfur component held thereby. Specifically, with the increase in the amount of the sulfur component held by the sulfur component holding agent 61, the sulfur component holding capacity of the sulfur component holding agent 61 decreases. Once the amount of the sulfur component held by the sulfur component holding agent 61 increases beyond a predetermined amount, therefore, the sulfur component releasing process is carried out for releasing the sulfur component from the sulfur component holding agent 61.

More specifically, first of all, the amount of the



sulfur component of the exhaust gas flowing into the sulfur component holding agent 61 is estimated from the amount of the fuel supplied to the intake path, the combustion chamber 5 and the exhaust path upstream of the sulfur component holding agent 61, to thereby estimate the amount of the sulfur component held in the sulfur component holding agent 61. In the case where the estimated amount of the sulfur component exceeds the predetermined amount, i.e. in the case where the sulfur component holding capacity of the sulfur component holding agent 61 is reduced, the operation of the internal combustion engine is controlled in such a way as to enrich the air-fuel ratio of the exhaust gas discharged from the internal combustion engine and, at the same time, to raise the temperature of the exhaust gas discharged from the internal combustion engine. As a result, the sulfur component releasing conditions for the sulfur component holding agent 61 are satisfied, and the sulfur component is released from the sulfur component holding agent 61 thereby to restore the sulfur component holding capacity of the sulfur component holding agent 61.

When the sulfur component is released from the sulfur component holding agent 61, however, the exhaust gas flowing out downstream of the sulfur component holding agent 61 contains a greater amount of the sulfur component than the exhaust gas discharged from the internal combustion engine. In the exhaust emission purification device 23 according to the first embodiment, therefore, the sulfur component releasing process for the sulfur component holding agent 61 is carried out in such a manner that the sulfur component releasing conditions are satisfied and the working position of the flow rate regulation valve 58 is changed to the bypass position to allow the greater proportion of the exhaust gas to flow into the bypass-side branch pipe 66d. As a result, as long as the sulfur component releasing conditions are

satisfied, substantially no exhaust gas flows into the NO<sub>x</sub> holding agent 62 and thus the exhaust gas containing a large amount of a sulfur component is prevented from flowing into the NO<sub>x</sub> holding agent 62.

5           As described above, the sulfur component holding agent 61 basically holds the sulfur component in the exhaust gas flowing thereinto, and when the sulfur component holding agent 61 releases the sulfur component held thereby, the exhaust gas is prevented from passing  
10           through the NO<sub>x</sub> holding agent 62. In this way, the exhaust gas containing the sulfur component can be prevented from flowing into the NO<sub>x</sub> holding agent 62, thereby making it possible to remove the sulfur component of the exhaust gas discharged from the internal  
15           combustion engine upstream of the NO<sub>x</sub> holding agent 62 in the exhaust gas.

          In the case where the reducing agent adding unit for adding the fuel to the exhaust gas flowing into the NO<sub>x</sub> holding agent 62 is arranged upstream of the flow rate  
20           regulation valve 68 in the exhaust gas, the fuel is undesirably attached to the flow rate regulation valve 68. Even in the case where the fuel in an amount proper for releasing and reducing the NO<sub>x</sub> held by the NO<sub>x</sub> holding agent 62 is injected from the reducing agent  
25           adding unit in order to carry out the rich spike against the NO<sub>x</sub> holding agent 62, therefore, the amount of the fuel actually flowing into the NO<sub>x</sub> holding agent 62 is different from the proper amount described above. In other words, it becomes impossible to properly regulate  
30           the amount of the fuel flowing into the NO<sub>x</sub> holding agent 62 when injecting the fuel from the reducing agent adding unit. Also, an increased amount of the fuel attached to the flow rate regulation valve 68 would prevent from the movement of the flow rate regulation valve 68, thereby  
35           making it impossible to control the flow rate regulation valve 68. Further, if the reducing agent adding unit is arranged upstream of the flow regulation valve 68 in the

exhaust gas, the distance from the reducing agent adding unit to the NO<sub>x</sub> holding agent 62 is generally lengthened, and the fuel is attached to the portion of the exhaust pipe ranging from the reducing agent adding unit to the NO<sub>x</sub> holding agent 62. This also makes it impossible to properly regulate the amount of the fuel flowing into the NO<sub>x</sub> holding agent 62 when injecting the fuel from the reducing agent adding unit.

In the exhaust emission purification device 23 according to the first embodiment of the invention, in contrast, as shown in Fig. 2, the reducing agent adding unit 70 is arranged downstream of the flow rate regulation valve 68 and upstream of the NO<sub>x</sub> holding agent 62 in the exhaust gas. Thus, the fuel, when injected from the reducing agent adding unit 70, is prevented from attaching to the flow rate regulation valve 68. As a result, the amount of the fuel flowing into the NO<sub>x</sub> holding agent 62, after being injected by the reducing agent adding unit 70, can be properly regulated, while at the same time the flow rate regulation valve 68 is not prevented from moving. Also, by arranging the reducing agent adding unit 70 immediately upstream of the NO<sub>x</sub> holding agent 62 or setting the injection from the reducing agent adding unit 70 in the direction toward the NO<sub>x</sub> holding agent 62, the amount of the fuel flowing into the NO<sub>x</sub> holding agent 62, after being injected from the reducing agent adding unit 70, can be regulated properly.

Next, an exhaust emission purification device 80 according to a second embodiment of the invention will be explained with reference to Figs. 3A-3C. The exhaust emission purification device 80 according to the second embodiment has a configuration similar to the exhaust emission purification device 23 according to the first embodiment, except that the configuration of the exhaust pipe 86 is different from that of the exhaust pipe 66 according to the first embodiment. Figs. 3A-3C are schematic views similar to Fig. 2. Fig. 3A shows the

flow rate regulation valve 88 in the first working position, Fig. 3B the flow rate regulation valve 88 in the second working position, and Fig. 3C the flow rate regulation valve 88 in at the intermediate working position. In these views, the arrows indicate the flow of the exhaust gas.

As shown in Figs. 3A-3C, according to the second embodiment, the exhaust pipe 86 includes trunk exhaust pipes 86a, 86e, and annular branch pipes (annular paths) 86c, 86d connected to the trunk exhaust pipes 86a, 86e. A casing 87 having the NO<sub>x</sub> holding agent 62 built therein is arranged on the annular branch pipes 86c, 86d. A branching portion 86b is arranged at the junction point between the trunk exhaust pipes 86a, 86e and the annular branch pipes 86c, 86d. Specifically, the annular branch pipes 86c, 86d branch from the branching portion 86b of the trunk exhaust pipes 86a, 86e and return to the branching portion 86b. The annular branch pipes 86c, 86d contain the reducing agent adding unit 90.

More specifically, the trunk exhaust pipes include the upstream partial exhaust pipe 86a upstream of the branching portion 86b in the exhaust gas and the downstream partial exhaust pipe 86e downstream of the branching portion 86b in the exhaust gas. The annular branch pipes include a first partial annular branch pipe 86c for connecting the branching portion 86b to one side of the NO<sub>x</sub> holding agent 62 and a second partial branch pipe 86d for connecting the branching portion 86b to the other side of the NO<sub>x</sub> holding agent 62. The upstream partial exhaust pipe 86a branches at the branching portion 86b into three exhaust pipes including the first partial annular branch pipe 86c, the second partial annular branch pipe 86d and the downstream partial exhaust pipe 86e. The upstream partial exhaust pipe 86a and the downstream partial exhaust pipe 86e are substantially aligned with each other, while the first partial annular branch pipe 86c and the second partial

annular branch pipe 86d branch off in opposite directions and substantially perpendicular to the trunk exhaust pipe 86a, 86e. Also, the reducing agent adding unit 90 is arranged in the first partial annular branch pipe 86c, in  
5 such a manner as to inject the fuel toward the NO<sub>x</sub> holding agent 62 in the exhaust gas flowing into the NO<sub>x</sub> holding agent 62 from the first partial annular branch pipe 86c.

The flow rate regulation valve 88 is arranged at the  
10 branching portion 86b. The operation of the flow rate regulation valve 88 is controlled by the step motor 89 connected to the output port 46 of the ECU 40 through the corresponding drive circuit 48. The flow rate regulation valve 88 is rotated continuously about the center of the  
15 branching portion 86b, and the angle  $\theta$  thereof changes with respect to the axial line of the trunk exhaust pipes 86a, 86e. Thus, it is possible to control the flow rate of the exhaust gas flowing into the annular branch pipes 86c, 86d and the direction in which the exhaust gas flows  
20 into the annular branch pipes 86c, 86d.

Especially, the flow rate regulation valve 88 according to the second embodiment is rotated roughly between three working positions of different angles. The three positions include the first working position shown  
25 in Fig. 3A, the second working position shown in Fig. 3B and the intermediate working position shown in Fig. 3C. In the case where the flow rate regulation valve 88 is in the first working position shown in Fig. 3A, substantially all the exhaust gas flowing into the  
30 branching portion 86b from the upstream partial exhaust pipe 86a flows into the first partial annular branch pipe 86c, and through the NO<sub>x</sub> holding agent 62 in one direction and then into the second partial annular branch pipe 86d, and returns again to the branching portion 86b.  
35 All the exhaust gas that has returned to the branching portion 86b from the second partial annular branch pipe 86d flows out to the downstream partial exhaust pipe 86e.

In the description that follows, the explanation assumes that the direction in which the exhaust gas flows through the annular branch pipes 86c, 86d and the NO<sub>x</sub> holding agent 62 in the way as described above is the forward direction.

In the case where the flow rate regulation valve 88 is in the second working position shown in Fig. 3B, on the other hand, substantially all the exhaust gas flowing into the branching portion 86b from the upstream exhaust pipe 86a flows into the second partial branch pipe 86d, and through the NO<sub>x</sub> holding agent 86 in the opposite direction to the direction in which the exhaust gas flows when the flow regulation valve 88 is located at the first working position, and then into the first partial annular branch pipe 86c, and returns again to the branching portion 86b. All the exhaust gas that has returned to the branching portion 86b from the first partial annular branch pipe 86c flows out to the downstream exhaust pipe 86e. In the description that follows, the explanation assumes that the direction in which the exhaust gas flows through the annular branch pipes 86c, 86d and the NO<sub>x</sub> holding agent 62 in this way as described above is the opposite direction.

Specifically, as described above, depending on the working position of the flow rate regulation valve 88, the exhaust gas that has flowed into the branching portion 86b from the upstream exhaust pipe 86a can flow in one or opposite direction through the annular branch pipes 86c, 86d having the NO<sub>x</sub> holding agent 62, and then can flow out to the downstream exhaust pipe 86e through the branching portion 86b.

As described above, according to the second embodiment, the flow of the exhaust gas passing through the NO<sub>x</sub> holding agent 62 can be changed between the forward direction and the opposite direction. Therefore, the imbalance of the NO<sub>x</sub> amount held depending on the positions by the NO<sub>x</sub> holding agent 62 can be relaxed and

the NO<sub>x</sub> holding agent can be efficiently utilized. Also, in the case where the NO<sub>x</sub> holding agent is carried in the filter as described later, the exhaust emission purification device according to the second embodiment  
5 can efficiently utilize the filter 62 by relaxing the imbalance in the amount of the trapped particulates depending on the positions in the filter. Further, by changing the direction of flow of the exhaust gas, the filter is prevented from clogging.

10 In the case where the flow rate regulation valve 88 is in the intermediate working position shown in Fig. 3C, substantially all the exhaust gas that has flowed into the branching portion 86b from the upstream exhaust pipe 86a flows into the downstream exhaust pipe 86e but not  
15 into the annular branch pipes 86c, 86d. Specifically, in the case where the flow rate regulation valve 88 is in the intermediate working position, the exhaust gas flows out to the downstream exhaust pipe 86e without passing through the NO<sub>x</sub> holding agent 62. According to the  
20 second embodiment, therefore, the intermediate working position of the flow rate regulation valve 88 constitutes a bypass position for bypassing the NO<sub>x</sub> holding agent 62 like the bypass position of the flow rate regulation valve 68 in the preceding embodiment. With the exhaust  
25 emission purification device 80 according to the second embodiment, the sulfur component is released from the sulfur component holding agent 61 by satisfying the sulfur component releasing conditions while, at the same time, regulating the flow rate regulation valve 88 in  
30 such a manner that the greater part of the exhaust gas flows through the exhaust path downstream of the branching portion 86b without flowing into the annular paths 86c, 86d.

Also, in the exhaust emission purification device 80  
35 according to the second embodiment, the reducing agent adding unit 90 is arranged in the first partial annular branch pipe 86c. In the case where the exhaust gas flows

in the forward direction through the NO<sub>x</sub> holding agent 62 and the annular branch pipes 86c, 86d, therefore, the exhaust gas with the fuel added thereto by the reducing agent adding unit 90 flows into the NO<sub>x</sub> holding agent 62.

5 In the case where the fuel flows in the opposite direction, however, the exhaust gas, even having the fuel added thereto from the reducing agent adding unit 90, is discharged without passing through the NO<sub>x</sub> holding agent 62. In the case where the rich spike operation is  
10 carried out for the NO<sub>x</sub> holding agent 62 in the exhaust emission purification device 80 according to the second embodiment, therefore, the flow rate regulation valve 88 is set at the first working position to assure the forward flow of the exhaust gas. Specifically, in the  
15 case where a single reducing agent adding unit 90 is arranged in the annular branch pipes 86c, 86d, the rich spike operation, if any, is carried out for the NO<sub>x</sub> holding agent 62 by adjusting the working position of the flow rate regulation valve 88 in such a manner that the  
20 fuel is added to the exhaust gas from the reducing agent adding unit 90 upstream of the NO<sub>x</sub> holding agent 62.

In the exhaust emission purification device 80 according to the second embodiment described above, a single reducing agent adding unit 90 is arranged in the  
25 annular branch pipes 86c, 86d. Alternatively, however, a single reducing agent adding unit may be arranged for each of the annular branch pipes 86c, 86d on both sides of the NO<sub>x</sub> holding agent 62, i.e. for each of the first partial annular branch pipe 86c and the second partial  
30 annular branch pipe 86d. As another alternative, a reducing agent adding unit may be arranged upstream of the flow rate regulation valve 88 in the exhaust gas. As a result, regardless of whether the exhaust gas flows in forward or opposite direction through the annular branch  
35 pipes 86c, 86d and the NO<sub>x</sub> holding agent 62, the rich spike operation can be carried out for the NO<sub>x</sub> holding agent 62 as long as the flow rate regulation valve 88 is



located at a working position other than the bypass position.

5       Next, the exhaust emission purification device according to a third embodiment of the invention will be explained with reference to Fig. 4. Fig. 4 is a schematic view similar to Fig. 3A showing the exhaust emission purification device 80 according to the second embodiment. As shown in Fig. 4, the exhaust emission purification device according to the third embodiment  
10       comprises a purification catalyst 91 built in the casing 92 downstream of the exhaust emission purification device 80 according to the second embodiment in the exhaust gas. The purification catalyst 91 is capable of purifying the exhaust gas flowing thereinto and arranged downstream of  
15       the downstream exhaust pipe 86e in the exhaust gas.

      According to the second embodiment described above, in the case where the working position of the flow rate regulation valve 88 is changed to the bypass position in order to release the sulfur component from the sulfur  
20       component holding agent 61, substantially all the exhaust gas fails to pass through the NO<sub>x</sub> holding agent 62 and therefore is discharged into the atmosphere without being purified thereby deteriorating the exhaust emission.

      According to the third embodiment of the invention,  
25       in contrast, the purification catalyst 91 is arranged downstream of the downstream exhaust pipe 86e in the exhaust gas. In the case where the sulfur component releasing process is performed for the sulfur component holding agent 61, therefore, the exhaust gas not  
30       substantially purified flows into the purification catalyst 91, which purifies the components other than the sulfur component of the exhaust gas. Even in the case where the NO<sub>x</sub> holding agent 62 is bypassed, to release the sulfur component from the sulfur component holding  
35       agent 61, therefore, the not-substantially-purified exhaust gas is prevented from being discharged into the atmosphere.

The purification catalyst 91 may be either a three-way catalyst not easily capable of holding the sulfur component of the influent exhaust gas or a particulate filter capable of trapping the particulates contained in the exhaust gas. Also, the exhaust emission purification device according to the third embodiment may be combined with the exhaust emission purification device according to the first embodiment. In this case, the purification catalyst 91 is arranged downstream of the confluence between the holding agent-side branch pipe 66c and the bypass-side branch pipe 66d.

Next, an exhaust emission purification device according to a fourth embodiment of the invention will be explained with reference to Fig. 5. Fig. 5 is a schematic view similar to Figs. 3A-3C and 4. The exhaust emission purification device according to the fourth embodiment comprises a reducing agent adding unit 93 in addition to the reducing agent adding unit 90 arranged in the annular branch pipes 86c, 86d upstream of the sulfur component holding agent 61 in the exhaust gas in the exhaust emission purification device according to the second embodiment.

With the exhaust emission purification device according to the fourth embodiment, in the case where the sulfur component held by the sulfur component holding agent 61 is required to be released, i.e. in the case where the sulfur component held by the sulfur component holding agent 61 exceeds a predetermined amount, the fuel is injected from the additional reducing agent adding unit 93 for releasing the sulfur component held by the sulfur component holding agent 61. The amount of the fuel injected into the exhaust gas from the additional reducing agent adding unit 93 is sufficient both to enrich the air-fuel ratio of the exhaust gas flowing into the sulfur component holding agent 61 and also to increase the temperature of the sulfur component holding agent 61 to higher than the sulfur component releasing

temperature by burning the injected fuel.

The exhaust emission purification device according to the fourth embodiment may be combined with the exhaust emission purification device according to the first  
5 embodiment and/or the third embodiment. In this case, the additional reducing agent adding unit is arranged upstream of the exhaust emission purification device according to the first and/or third embodiment in the exhaust gas.

10 In the embodiments described above, the fuel to be injected from the reducing agent adding units 70, 90, 93 is stored in a fuel tank (an additional fuel tank, not shown) different from the tank for the fuel supplied to the combustion chamber 5 of the internal combustion  
15 engine. As a result, the fuels from the two tanks are not mixed before being supplied to the combustion chamber 5 of the internal combustion engine or before being injected from the reducing agent adding unit 70, 90, 93. A fuel lower in sulfur component concentration than the  
20 fuel supplied to the internal combustion engine is stored in the additional fuel tank for the fuel to be injected from the reducing agent adding units 70, 90, 93, respectively.

25 As an alternative, in the embodiments described above, the fuel to be injected from the reducing agent adding unit 70, 90, 93 is changed in quality from the fuel supplied to the combustion chamber 5 of the internal combustion engine. Specifically, the fuel to be injected from the reducing agent adding unit 70, 90, 93 is  
30 generated by desulfurizing the fuel supplied to the combustion chamber 5 of the internal combustion engine. The fuel may be desulfurized either before or after the fuel is supplied to the fuel tank. In the case where the fuel is desulfurized before being supplied to the fuel  
35 tank, the desulfurized fuel is stored in the additional fuel tank.

In the case where the fuel is desulfurized after

being supplied to the fuel tank, on the other hand, the internal combustion engine is equipped with a desulfurizing unit for desulfurizing the fuel. In this case, there is provided only one fuel tank from which two  
5 fuel supply paths are formed including a fuel supply path for supplying the fuel to the combustion chamber of the internal combustion engine and a fuel supply path for supplying the fuel to the reducing agent adding unit. The desulfurizing unit is arranged in the fuel supply  
10 path for supplying the fuel to the reducing agent adding unit.

Actually, however, any fuel can be used for injection from the reducing agent adding unit as far as the oxygen concentration of the exhaust gas flowing into  
15 the NO<sub>x</sub> holding agent 62 can be decreased and the NO<sub>x</sub> released from the NO<sub>x</sub> holding agent can be reduced. Light oil, methane, etc. are some examples of the fuel.

In the embodiments described above, the NO<sub>x</sub> holding agent 62 may be carried on the particulate filter capable  
20 of trapping the particulates in the exhaust gas flowing thereinto. Further, this particulate filter may include an active oxygen generating agent for continuously oxidizing and removing the trapped particulates, in the mechanism described later. The active oxygen generating  
25 agent, like the NO<sub>x</sub> holding agent 62 in the embodiments described above, can hold and release the sulfur component of the exhaust gas flowing thereinto. The ability of the active oxygen generating agent to remove the particulates is reduced by holding the sulfur  
30 component.

A mechanism for purifying the exhaust gas by the particulate filter (hereinafter referred to as the filter) or especially, the action thereof for removing the particulates from the exhaust gas according to this  
35 invention will be explained below. In Figs. 6A and 6B, an explanation will be given about a case in which platinum (Pt) is used as a precious metal catalyst and

potassium (K) as an active oxygen producing agent. A similar action of removing the particulates can be performed even when using another precious metals, alkali metals, alkali earth metals, rare earth or transition metals.

Figs. 6A and 6B are enlarged views schematically showing the surface of a carrier layer formed on the surface of a filter partition wall and the microporous surface of the partition wall. In Figs. 6A and 6B, numeral 95 designates platinum particles, and numeral 96 a carrier layer containing an active oxygen producing agent such as potassium.

In the case where the air-fuel ratio of the exhaust gas flowing into the filter is lean,  $\text{NO}_x$ , or especially NO and  $\text{NO}_2$ , is produced in the combustion chamber 5. Therefore, the exhaust gas contains  $\text{NO}_x$ . In this way, the exhaust gas containing an excess oxygen and  $\text{NO}_x$  flows into the filter.

Once the exhaust gas flows into the filter, as shown in Fig. 6A, the oxygen in the exhaust gas adheres to the surface of platinum in the form of  $\text{O}_2^-$  or  $\text{O}^{2-}$ . The NO in the exhaust gas, on the other hand, reacts with  $\text{O}_2^-$  or  $\text{O}^{2-}$  on the surface of the platinum and becomes  $\text{NO}_2$  ( $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ ). Then, part of the  $\text{NO}_2$  in the exhaust gas and the  $\text{NO}_2$  thus produced are absorbed in the active oxygen producing agent 96 while being oxidized on the platinum, and, while bonding with the potassium, diffuses in the active oxygen producing agent 96 in the form of nitrate ions ( $\text{NO}_3^-$ ) as shown in Figs. 6A and 6B to thereby generate a nitrate ( $\text{KNO}_3$ ). In other words, the oxygen in the exhaust gas is held in the active oxygen producing agent 96 in the form of nitrogen ions.

Particulates mainly composed of carbon (C) are produced in the combustion chamber. Thus, the exhaust gas contains these particulates. The particulates in the exhaust gas, while flowing in the filter, come into contact with and adhere to the surface of the active

oxygen producing agent 96 as shown in Fig. 6B.

Once the particulates 97 are adhered to the active oxygen producing agent 96, a concentration difference develops between the surface of the active oxygen  
5 producing agent 96 and the interior thereof. The active oxygen producing agent 96 has held therein oxygen in the form of nitrate ions, and this held oxygen tends to move toward the contact surface between the particulates 97 and the active oxygen producing agent 96. As a result,  
10 the nitrate ( $\text{KNO}_3$ ) formed in the active oxygen producing agent 96 is decomposed into O and NO, of which O moves toward the surface of the active oxygen producing agent 96 while NO is released out from the active oxygen producing agent 96. The NO released out in this way is  
15 oxidized on the downstream platinum by the mechanism described above, and held again as nitrate ions in the active oxygen producing agent 96.

The oxygen O moving toward the contact surface between the particulate 97 and the active oxygen  
20 producing agent 96, which is oxygen formed by decomposition from a chemical compound such as a nitrate ( $\text{KNO}_3$ ), has unpaired electrons and constitutes active oxygen having a very high reactivity. Once this active oxygen is brought into contact with the particulates 97,  
25 the particulates 97 are oxidized in a short time (several seconds to scores of minutes) and completely removed without generating a luminous flame. In this way, the particulates 97 are oxidized away and rarely accumulate on the filter.

30 In this specification, the term "hold" is to be understood to mean either "absorb" or "adsorb". The term " $\text{NO}_x$  holding agent", therefore, means both " $\text{NO}_x$  absorbent" and " $\text{NO}_x$  adsorbent". The former accumulates  $\text{NO}_x$  in the form of nitrate or the like, and the latter  
35 adsorbs  $\text{NO}_x$  in the form of  $\text{NO}_2$  or the like. Also, the term "release" from the  $\text{NO}_x$  holding agent is to be understood to mean "discharge" as an antonym of "absorb",

or "release" as an antonym of "adsorb".

While the invention has been described by reference to specific embodiments chosen for purposes of illustration, it should be apparent that numerous  
5 modifications could be made thereto by those skilled in the art without departing from the basic concept and scope of the invention.